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Non-isothermal pyrolysis of torrefied stump – A comparative kinetic evaluation

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HIGHLIGHTS

- The first pyrolysis kinetic study of torrefied stump.
- Three pseudo-components model with $n \neq 1$ is the most suitable for the kinetics.
- The torrefied stump has higher activation energy than the untreated stump.

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ABSTRACT

The pyrolysis of native and torrefied stump materials was studied in the kinetic regime by means of a thermogravimetric analyzer operated in the non-isothermal fashion. Three different kinetic models applicable to biomass pyrolysis were evaluated for the collected data, which include a single-reaction model, two three pseudo-components models, and a distributed activation energy model (DAEM). It was shown that the single-reaction model was not suitable to simulating stump biomass pyrolysis. The other models including the three pseudo-components model with $n = 1$ and $n \neq 1$, and the DAEM demonstrated very good fits between simulated and experimental curves. However, the three pseudo-components model with $n \neq 1$ is recommended as the most suitable for simulation and prediction of kinetic behaviour of slow pyrolysis for both untreated and torrefied stump, considering that it offers the best fits to the experimental data and that the generated reaction orders are realistic, being slightly higher than unity. It appears that the torrefied stump has higher activation energy than its native material. The activation energy predicted for the native stump pyrolysis is in the range of 105.2–108.9 kJ/mol, 183.5–183.6 kJ/mol, and 40.3–48.01 kJ/mol for hemicelluloses, celluloses, and lignin, respectively. That for pyrolysis of the stump torrefied at 200 °C is 105.13–111.19 kJ/mol, 183.68–185.79 kJ/mol, and 40.49–50.70 kJ/mol, respectively.

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1. Introduction

Biomass resources have been used by mankind for a very long time in order to meet its primary energy needs and to power human development. With increasing concerns of human impacts on the environment and climate, biomass is once again considered as an important energy source to meet a significant portion of the increasing energy demand in the modern world. The challenges today in using biomass as fuel are various, but can be best related to scale and density, among which the scale of energy demand by far exceeds all the needs in past [1]. Both the increasing world population and the energy intensity of modern life compound the high demand for energy as never before. Consequently, the extraction of biomass from forest and agriculture for use as fuel has become a common practice in various countries and increased the burden on the soil. In addition to the problems of land-use conflict and increased food price, today people even fear the problem of competing for wood between the paper and energy industries [2].

One way to meet the growing demand of forest biomass for energy application, without increasing the annual harvesting volume of stem wood, is to utilize tree stump, which may be defined as all belowground and aboveground wood and bark mass of a tree beneath the merchantable timber cross-section. It is reported that when tree stumps and small round-wood from thinning are used to replace fossil fuels, the potential CO_2 reduction will be about

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Nomenclature

Abbreviation

DAEM	distributed activation energy model
TG	thermogravimetry
TGA	thermogravimetric analysis
DTG	derivative thermogravimetry

Symbols

A	pre-exponential factor
E_a	activation energy
E_o	mean activation energy
$f(E)$	distribution function of activation energy
T	absolute temperature, K
R	universal gas constant, 8.314 J mol^{-1} K^{-1}
n	reaction order
t	time of conversion
m_0	the initial mass
m_f	the final residual mass
m_t	the mass of the sample at time t
α	degree of conversion
x	mass fraction of released volatiles
V	accumulated volatiles produced
V^*	final accumulated volatiles produced
β	heating rate
σ	standard deviation

Subscript

i	ith component

four times as great as when only logging residues are used with a traditional chip system [3]. However, tree stumps have not yet been recognized as a bioenergy resource. For these reasons, a study on torrefaction of Norway spruce stump wood for energy application has been performed [4]. Torrefaction is a pretreatment process for biomass fuels, in which the biomass is slowly heated to 200–300 °C in the absence or little contact with oxygen [5–7]. Torrefaction alters the chemical structure of biomass hydrocarbon and increases its carbon content while reducing its oxygen [5,6]. In addition, torrefaction increases the heating value and grindability of the biomass and makes the biomass hygroscopic. These attributes thus enhance the market value of biomass fuel for energy supply and transportation.

Due to the aforementioned benefits, torrefaction had been being considered for effective utilization of biomass as a clean and convenient solid fuel [7]. A significant effort has been made to understand better the effects of the torrefaction conditions on the yield and fuel properties of the solid product. However, the behaviour of torrefied biomass during pyrolysis, gasification or combustion has received little attention [8], considering that changes in chemical structure of biomass by torrefaction would cause changes in the reaction mechanisms and kinetics of further thermochemical conversions of biomass, which include pyrolysis, gasification, and combustion [8].

Apart from combustion and gasification, the kinetics of biomass pyrolysis is of great importance in the context of energy recovery [9]. Modelling the processes of pyrolysis, gasification, and combustion of biomass requires the kinetics of mass loss and gas evolving. Kinetic evaluation of the data obtained from isothermal or non-isothermal thermogravimetric analysis (TGA) of biomass fuels is needed for the design of thermochemical conversion system. For these reasons, past research in the field was very active with numerous reports in open literature sources, which can be found in a recent review [10]. However, kinetic studies which take into account the pyrolysis of hemicellulose, cellulose and lignin, already developed for biomass, have not yet been fully applied to torrefied fuels [8]. Only few attempts [8,11,12] can be found in the open literature. Ren et al. [12] described the thermogravimetric (TG) curves in nitrogen of torrefied sawdust. A one-step global kinetic model was employed for extracting the kinetic parameters from the derivative thermogravimetric (DTG) curves. Broström et al.[8] employed a multi pseudo-components kinetic model built on the basis of n-order independent parallel reactions to study the thermal decomposition of torrefied spruce wood chips in nitrogen, as well as in air. Furthermore, Tapasvi et al. [13] established even more detailed and more complex model, mainly based on the distributed activation energy model (DAEM), to describe better the pyrolysis kinetics of biomass, which is claimed suitable for pyrolysis of torrefied biomass as well.

Biomass pyrolysis is a very complex process due to differences in reactivity of biomass constituents. Different chemical reactions associated with the thermal decomposition of each biomass constituent may occur, which lead to very different levels of modelling. A recent review [10] of biomass pyrolysis kinetics indicated that, while some workers tried extreme simplifications, others used elaborate mechanisms to explain several details. In kinetic modelling and simulation, however, Levenspiel [14] argued that it is essential to select a kinetic model which reasonably represents the physical phenomenon under investigation without too many mathematical complexities. It is of little use to select a model which very closely mirrors reality but which is so complicated that we cannot do anything with. Having this argument in mind, perhaps, a study on pyrolysis of biomass with a comparison of different kinetic models was reported by Hu et al. [15]. However, this work was performed for untreated biomass only and the DAEM was not included. This along with the reasons discussed above suggested a need to perform a similar study for torrefied fuels and to include the DAEM for kinetic evaluation. Therefore the study reported in this present paper was carried out for Norway spruce stump chips, untreated and torrefied, using a TG analyzer operated in the non-isothermal fashion. Apart from the model-free Ozawa method, three different kinetic models applicable to biomass pyrolysis were evaluated for the collected data, which were single-reaction model, three-pseudo-component model, and DAEM. The objective of the present study was manifold. The first objective was to confirm the study by Hu et al. [15] (Sections 4.1–4.3). The second was to compare the kinetic behaviour between untreated and torrefied stump chips (Sections 4.3–4.5). The third, being the primary objective of the present study, was to identify among the models based on independent parallel reactions the most suitable one for the kinetic evaluation of torrefied stump fuels, from which the kinetic parameters were extracted (Sections 4.3–4.5).

2. Kinetic modelling

Despite the complexity, the process of biomass pyrolysis may be represented by a simplified kinetic model which involves lumping (pseudo) [16,17] of the complicated multiple reactions together as a single first- or nth-order reaction according to the following global reaction scheme: Solid biomass → Char + Volatiles.

For this scheme, the kinetic equation of common type can be written as the following

$$\frac{d\alpha}{dt} = A\exp\left(\frac{-E_a}{RT}\right)f(\alpha) \tag{1}$$

where α and t is the degree and time of biomass conversion, A the pre-exponential factor, E_a the activation energy, T the absolute temperature, and R the universal gas constant (8.314 J mol^{-1} K^{-1}).

$$\alpha = \frac{m_o - m}{m_o - m_f} \tag{2}$$

where m_0 is the initial mass, m_f is the final residual mass and m is the mass of the sample at time t. The conversion function $f(\alpha)$ in Eq. (1) can take different forms, depending on the reaction mechanism of the pyrolysis, which can be found in the literature [18]. Various methods for estimating the kinetic parameters in these models have been presented [16], of which only the Ozawa method [19,20] allows to determine the activation energy of biomass pyrolysis [15] using non-isothermal TG analysis with no need of information about the reaction mechanism. The activation energy calculated by Ozawa method would indicate whether or not the TG experiments were studied in the kinetic regime.

2.1. Ozawa method

For non-isothermal experiments conducted with a linear heating rate $\beta = \frac{dT}{dt}$ Eq. (1) can be re-written to obtain Eq. (3),

$$\frac{d\alpha}{dt} = \left(\frac{A}{\beta}\right)\exp\left(\frac{-E_a}{RT}\right)f(\alpha) \tag{3}$$

Integrating both sides of Eq. (3) leads to Eq. (4),

$$g(\alpha) = \left(\frac{A}{\beta}\right)\int_{T_0}^{T}\exp\left(\frac{-E_a}{RT}\right)dT = \left(\frac{AE_a}{\beta R}\right)p(u) \tag{4}$$

where $p(u) = \int_{\infty}^{u} -\left(\frac{e^{-u}}{u^2}\right)du$ and $u = \frac{E_a}{RT}$

In this method, it is assumed that A, $f(\alpha)$ and E_a are independent of T; and A, E_a are independent of α. With these assumptions, Eq. (4) can be integrated to obtain a logarithmic form in Eq. (5),

$$g(\alpha) = \log\left(\frac{AE_a}{R}\right) - \log\beta + \log\left[p\left(\frac{E_a}{RT}\right)\right] \tag{5}$$

Further, Doyle's approximation [21] can be used to simplify the temperature integral $p(u)$. Then, Eq. (5) can be re-written to obtain Eq. (6),

$$\log\beta = \log\left(\frac{AE_a}{Rg(\alpha)}\right) - 2.3125 - 0.4567\left(\frac{E_a}{RT}\right) \tag{6}$$

According to Eq. (6), at a constant conversion (α), the plot of $\log\beta$ versus T^{-1} should be a straight line, of which the slope can be used for calculation of the activation energy (E_a).

2.2. Single-reaction model

For the single-reaction model with a general n-order reaction, the rate law can be represented by Eq. (7)

$$\frac{d\alpha}{dt} = A\exp\left(\frac{-E_a}{RT}\right)(1-\alpha)^n \tag{7}$$

where n is the reaction order and the other terms have been defined earlier.

In general, this model can be tested with experimental data for determination for the kinetic parameters (E_a, A, and n) using the non-linear least square fitting technique. It can also be tested with the data employing the mean value of the activation energies calculated by Ozawa method at various conversion degrees (α), searching for the pre-exponential factor (A) and the reaction order (n) only [15].

2.3. Three pseudo-components model

Biomass material may be considered to consist of three main components including hemicellulose, cellulose and lignin. Their behaviours in a thermal process such as thermal pyrolysis are different to one another. Generally, hemicellulose is the most thermal sensitive, which degrades in the temperature range of 200–300 °C. Cellulose starts decomposing from around 300 °C. The thermal degradation of lignin is generally within a broad range of temperatures. Therefore, it is difficult to use the single-reaction model for simulation the thermal decomposition of biomass.

Quite recently, a three pseudo-components model, or a model with three independent parallel reactions, has been proposed to overcome the limitation of the single-reaction model in simulating the global one-step reaction scheme of biomass pyrolysis [22] as it can represent for three main components of biomass. More recently, the model was successfully tested for the slow pyrolysis of several Chinese biomass materials with reaction order n equal and different from unity [15].

In the present study, the partial degradation rate of three lignocellulosic components of stump is presented by Eq. (8)

$$\frac{d\alpha_i}{dt} = A_i\exp\left(\frac{-E_{a,i}}{RT}\right)f(1-\alpha_i) \quad i = 1,2,3 \tag{8}$$

The overall conversion rate of degradation for stump is the sum of the partial conversion rates

$$\frac{d\alpha}{dt} = \sum_{1}^{3} c_i\frac{d\alpha_i}{dt} \tag{9}$$

where c_i indicates the contribution factor of each component. The 1st, 2nd, and 3rd components were assigned to hemicellulose, cellulose and lignin, respectively.

Depending on the reaction order, there are two types of three-pseudo-component model. One assumes that $n = 1$, the other uses n different from 1 [15,23].

2.4. Distributed activation energy model

The distributed activation energy model (DAEM) is believed to be proposed first by Pitt [24], which is presented by a series of parallel first-order reactions with different activation energy values but the same pre-exponential factor. The nth-order DEAM was later developed by Braun and Burnham [25]. A general equation for DAEM is shown below:

$$1 - \frac{V}{V^*} = \int_0^{\infty}\exp\left(-A\int_0^t e^{\frac{-E_a}{RT}}dt\right)f(E)dE \tag{10}$$

In Eq. (10), the term $f(E)$ is the distribution function of activation energy. Several forms of $f(E)$ are reported in the literature including Gaussian, Weibull, and Gamma distribution [26]. Among these functions, the Gaussian representing a mean activation value (E_0) and its standard deviation σ according Eq. (11) is the most widely used,

$$f(E) = \frac{1}{\sigma\sqrt{2\pi}}\exp\left(-\frac{(E-E_0)^2}{2\sigma^2}\right) \tag{11}$$

The most challenging in applying the DAEM to studying the thermal degradation of biomass is that this model has a double-layer integral and one variable (E) going from 0 to infinite, which could not be computed directly. Several simplifications [27–31] were proposed to reduce the complexity of Eq. (10) in practical calculation.

In the present study, the calculation proposed by Cai and Liu [32] was adopted. Eq. (12) was employed to determine the mass fraction of released volatiles (x). For simplicity in calculation, the reaction order of unity was chosen.

$$1 - x_i = \int_0^\infty \exp\left(-\frac{A_i}{\beta}\int_0^T e^{\frac{-E_{a,i}}{RT}}dT\right)f(E)dE \quad i = 1,2,3 \tag{12}$$

Three series of kinetic parameters including E_0, σ, A, and c were determined for three components of biomass. It should be noticed that the DAEM was first applied for modelling the released volatiles. Thus it can be easy to model the remaining solids, which is recorded in a TG experiment. However, when the TGA data are differentiated to obtain DTG data, some serrations will occur and therefore it needs to smooth the TGA data in a separated step after searching for kinetic values.

3. Materials and methods

3.1. Material and experimental methods

All of the biomass materials used for the TG analyses of this study were obtained from our previous study (part one of the project) on torrefaction of Norway spruce stump for energy application, in comparison with poplar wood and wood fuel chips from the industry [4]. For the present study, only stump chips were used as feedstock, of which the fuel properties are presented in Table 1. The TG experiments were carried out mainly for untreated stump and the stump torrefied at 200, 250, and 300 °C for 30 min. These three torrefied stump samples were all extensively tested with the TGA and kinetic evaluations using the two models based on independent parallel reactions. The kinetic parameters were extracted and presented for all the collected data, but only the fitting results from the stump torrefied at 250 °C for 30 min were graphically presented for demonstration. Further details about the fuel properties and torrefaction conditions can be found in our previous report [4].

A thermogravimetric analyzer from Perkin Elmer (Pyris 1) was employed for studying non-isothermal decomposition of torrefied biomass in nitrogen. The nitrogen flow was introduced into the TGA at a volumetric flow rate of 40 ml/min for all runs. The initial mass of sample for each run was in the range of 6–8 mg. The temperature range was within 25–600 °C. The heating rates of 10 K/min, 20 K/min, or 40 K/min were employed.

3.2. Non-linear least square fitting method

In this present study, non-linear least square method was employed for curve fitting, of which the objective function to minimize is given in Eq. (13)

$$S = \sum_{i=1}^{N}\left[\left(\frac{d\alpha_i}{dt}\right)_{\exp} - \left(\frac{d\alpha_i}{dt}\right)_{cal}\right]^2 \tag{13}$$

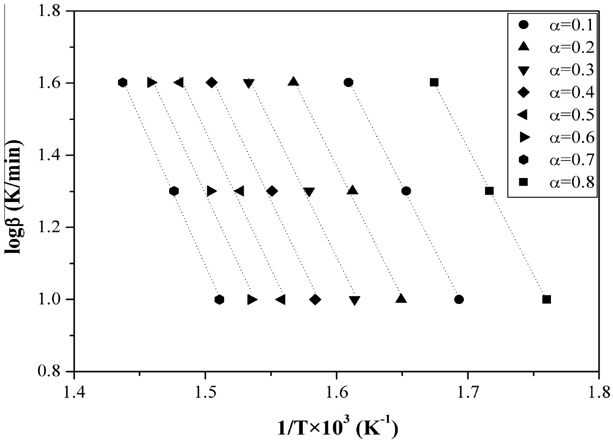

Fig. 1. Determination of activation energy for untreated stump by Ozawa method.

Table 2
Data extracted from Ozawa method.

α	E_a (kJ/mol)	A (s^{-1})
0.1	128.02	5.30E+09
0.2	130.21	2.87E+09
0.3	133.11	2.52E+09
0.4	135.09	2.07E+09
0.5	137.44	1.97E+09
0.6	139.44	1.86E+09
0.7	141.89	1.95E+09
0.8	148.46	4.09E+09
Average value	136.71	2.83E+09

where $\left(\frac{d\alpha_i}{dt}\right)_{\exp}$ and $\left(\frac{d\alpha_i}{dt}\right)_{cal}$ represent the experimental and calculated conversion rates, N is the number of experimental points. The fit between measured and simulated values is defined by Eq. (14) [33]:

$$\text{Fit }(\%) = \left(1 - \frac{\sqrt{\frac{S}{N}}}{\left[\left(\frac{d\alpha_i}{dt}\right)_{\exp}\right]_{\max}}\right).100\% \tag{14}$$

4. Results and discussions

4.1. Activation energy determined by Ozawa method

The method developed by Ozawa for mechanism free determination of the activation energy was first carried out for un-torrefied stump samples. Fig. 1 shows the plots of $\log\beta$ versus T^{-1}, which are straight lines. The slopes and intercepts of the lines were used to calculate the activation energy (E_a) and the pre-exponential factor (A) at different conversion degree α being from 0.1 to 0.8, of which the results are presented in Table 2.

From Table 2 it can be noted that the activation energy varies from 128.02 to 148.46 (kJ/mol) and the average value is 136.71

Table 1
Proximate and ultimate analyses of the feedstock material.

Sample	HHV (MJ/kg)	Proximate		Ultimate**			
		Ash content** (wt%)	Moisture content* (wt%)	C (wt%)	H (wt%)	N (wt%)	O (wt%)
Spruce stump chip	20.55	8.14	7.06	49.4	5.8	0.1	40.9

HHV = higher heating value.
* Wet basis.
** Dry basis.

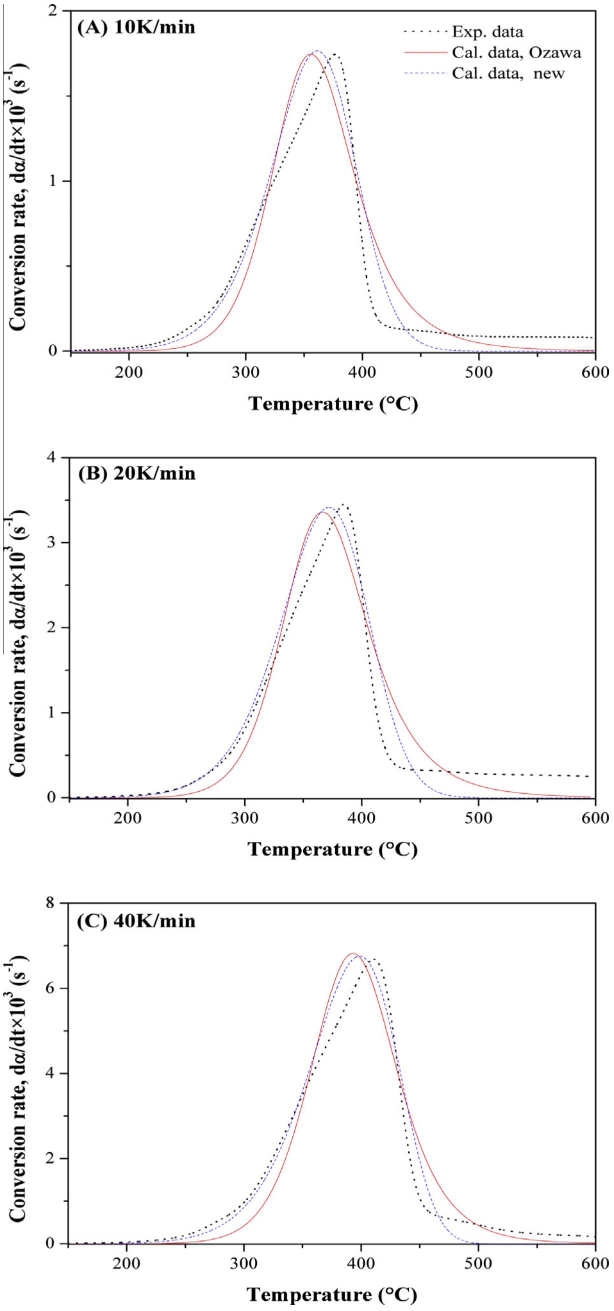

Fig. 2. Single-reaction model for pyrolysis of untreated stump at the heating rate of: (A) 10; (B) 20; (C) 40 K/min.

Table 3
Kinetic parameters and fit quality of the test for the single-reaction model.

	Heating rate	E_a (kJ/mol)	A (s^{-1})	n	Fit (%)
Ozawa method	10 K/min	136.71	1.46E+09	2.19	90.87
	20 K/min		1.82E+09	2.19	91.56
	40 K/min		1.23E+09	1.88	92.13
None Ozawa	10 K/min	97.26	4.87E+05	1.22	92.85
	20 K/min	95.46	4.87E+05	1.17	92.49
	40 K/min	95.91	4.87E+05	1.03	94.52

(kJ/mol). In addition, the pre-exponential factor varies within the range from 1.86E+09 to 5.30E+09 (s^{-1}) and the average value is 2.83E+09 (s^{-1}).

The relatively low average value (136.71 kJ/mol) of the calculated activation energy for the native untreated stump wood can be attributed to the relatively low hemicelluloses and high lignin content of the material as discussed in our previous report [4]. Nevertheless, this may raise a question about whether or not the TG experiments have been carried out in the regime of chemical reaction kinetics [34]. Therefore, extra TG experiments were carried out in the same conditions for the untreated poplar wood and wood fuel chips samples. It appears that the calculated average value of activation energy for the poplar and fuel chips are considerably higher than that of stump, being 161.60 and 174.04 kJ/mol, respectively. This indicates that the experiments were in the kinetic regime.

4.2. Test of the single-reaction model

In this test, two methods were employed with or without utilization of the data obtained from the Ozawa estimation. First, the average activation energy obtained by Ozawa method in the previous section was utilized to search for the pre-exponential factor (A) and reaction order (n). The model fitting was tested for the TG data collected from the pyrolysis of untreated stump at three different heating rates and the results are presented in Fig. 2, from which the kinetic parameters are extracted and tabulated in Table 3. As can be seen from the data in Fig. 2 and Table 3 the fit of the simulated curves using the activation energy calculated by Ozawa method to the experimental data is poor, varying within 90–92%. For the non-Ozawa simulation, the new values obtained for E_a, A, n are all smaller than that of Ozawa-related simulation, with slightly better fits being within 92–94%. Overall, the best fits

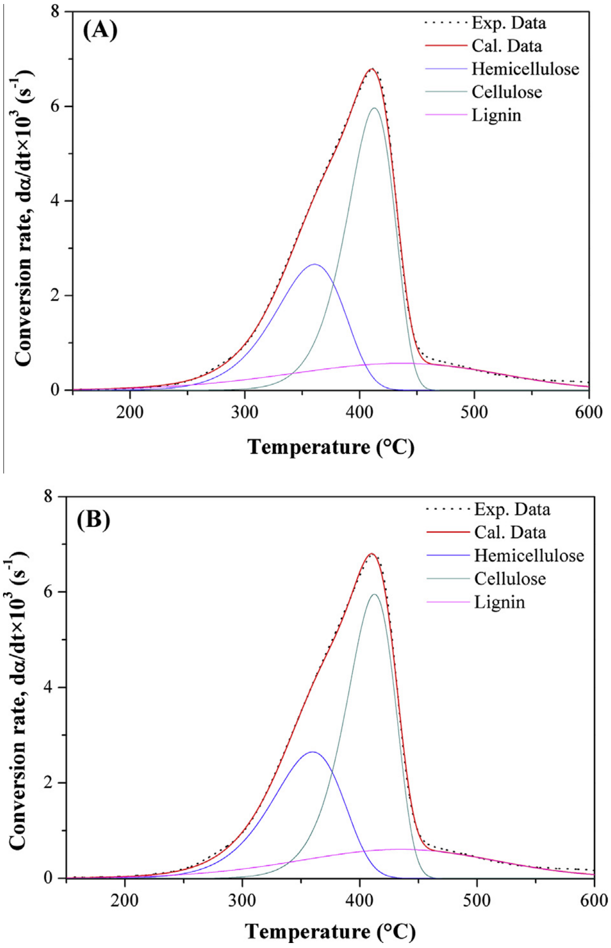

Fig. 3. Three-pseudo-component simulation for native stump with (A) $n = 1$; (b) $n \neq 1$ (heating rate = 40 K/min).

observed from this test are very poor and the extracted kinetics parameters are not realistic. Therefore, it is believed that the single-reaction model is not suitable for describing the pyrolysis of stump material, which gave no motivation for further test of the model for the torrefied samples.

4.3. Test of the three pseudo-components model

The three pseudo-components model was tested for both native (untreated) and torrefied stump samples, with $n = 1$ and $n \neq 1$. Results from the tests are presented in Figs. 3 and 4 for native and torrefied samples, respectively. In addition, the kinetic parameters extracted from the fitting are presented in Table 4.

As can be seen from the DTG curves in Fig. 3 (for untreated stump at the TG heating rate of 40 K/min) and Fig. 4 (for stump torrefied at 250 °C and the TG heating rate of 40 K/min) the model fits very well to the experimental data for both cases with $n = 1$ and $n \neq 1$. Comparing the fits of the simulated curves to the experimental curves in the two figures, it is observed that the fit in Fig. 3 is slightly better than that in Fig. 4, which is confirmed by the numerical values presented in Table 4.

On the other hand, only very small improvements in fit quality are observed for the model with $n \neq 1$ compared to that with $n = 1$, though it is hard to recognize the differences by visual inspections. Numerical data in Table 4 shows that the difference in fit quality for untreated stump at the heating rate of 10 K/min is 0.21% and the changes in value of the kinetic parameters including the activation energy, the pre-exponential factor and the contribution factor are also small between two cases with regard to the reaction order.

4.4. Test of the distributed activation energy model

It is worthwhile to remark that, while the three pseudo-components model generates constant E_a values for each component in the whole decomposition process, the DAEM gives more information about the actual activation energy, which is known as a temperature dependent parameter. The benefit of the DAEM is that it

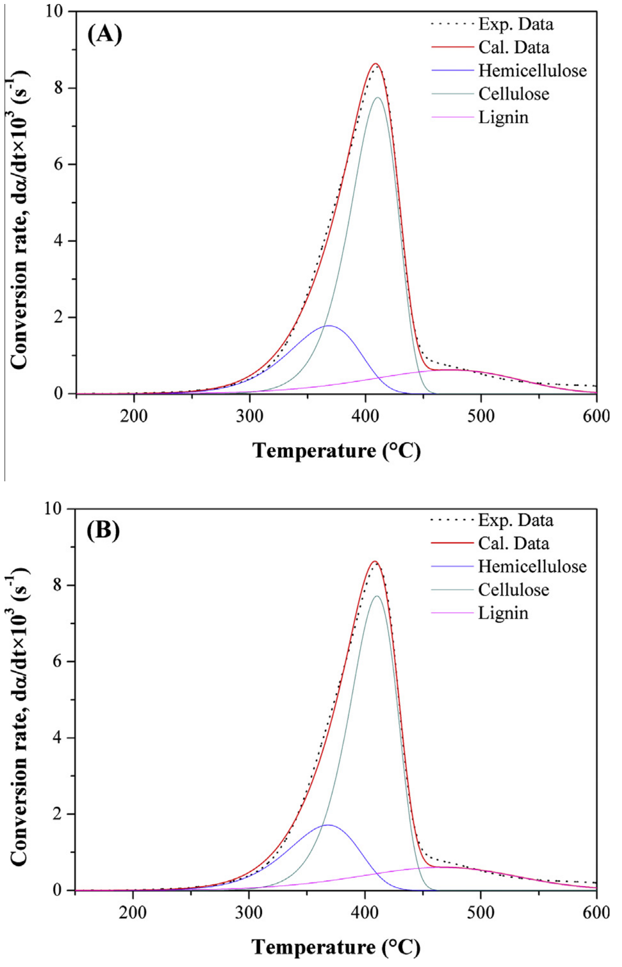

Fig. 4. Three-pseudo-component simulation for stump torrefied at 250 °C for 30 min, with (A) $n = 1$; (B) $n \neq 1$ (heating rate = 40 K/min).

Table 4
Extracted data from the three pseudo-components model.

Sample	Three-pseudo-component model $n = 1$				Three-pseudo-component model $n \neq 1$				
	E_a (kJ/mol)	A (s^{-1})	c	Fit (%)	E_a (kJ/mol)	A (s^{-1})	c	n	Fit (%)
US (10 K/min)	108.29	1.61E+07	0.33	98.86	108.4	1.61E+07	0.35	1.16	99.07
	185.12	6.56E+12	0.48		185.18	6.56E+12	0.46	1.01	
	38.54	9.29E−01	0.19		38.49	9.87E−01	0.2	1.37	
US (20 K/min)	105.32	1.01E+07	0.33	98.90	105.17	1.01E+07	0.33	1.01	98.92
	192.44	3.01E+13	0.44		192.30	3.01E+13	0.45	1.04	
	44.99	3.98E+00	0.23		45.05	3.95E+00	0.22	1.01	
US (40 K/min)	105.32	1.01E+07	0.32	99.34	105.17	1.01E+07	0.32	1.01	99.35
	183.58	3.01E+12	0.49		183.50	3.01E+12	0.49	1.01	
	40.24	5.91E+00	0.20		48.01	2.60E+01	0.19	1.17	
TS 200 °C (40 K/min)	105.36	1.01E+07	0.31	99.08	105.13	1.01E+07	0.31	1.01	99.29
	183.78	3.01E+12	0.54		183.68	3.01E+12	0.55	1.01	
	40.95	5.54E+00	0.15		58.91	1.33E+02	0.14	1.13	
TS 250 °C (40 K/min)	106.65	1.01E+07	0.21	98.61	106.62	1.01E+07	0.21	1.01	98.60
	182.95	3.01E+12	0.63		182.89	3.01E+12	0.63	1.01	
	66.73	4.49E+02	0.15		66.18	4.49E+02	0.16	1.17	
TS 300 °C (40 K/min)	–	–	–	97.32	–	–	–	–	97.31
	182.33	3.01E+12	0.74		182.32	3.01E+12	0.74	1.01	
	79.63	3.57E+03	0.26		79.40	3.57E+03	0.26	1.15	

US: untreated stump, TS: torrefied stump.

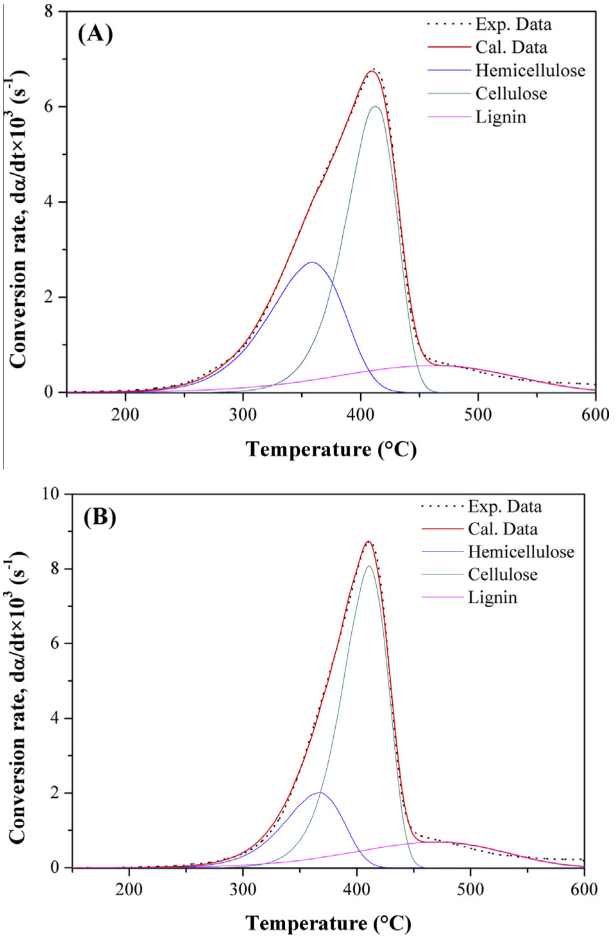

Fig. 5. DAEM simulation for pyrolysis of stump (A) untreated; (B) torrefied at 250 °C for 30 min (TG heating rate of 40 K/min).

shows a mean activation energy value (E_0) and its deviation (σ), therefore the actual activation energy varies in the range of ($E_0 - \sigma$) to ($E_0 + \sigma$). However, the model requires a more complex procedure to determine the kinetic parameters. On the other hand, it should also be remarked that the DAEM in this work was tested with the reaction order $n = 1$ only, and therefore the comparison between the DAEM and the three pseudo-components model will consider only for $n = 1$.

The DAEM curve fittings for untreated stump (heating rate of 40 K/min) and stump torrefied at 250 °C are demonstrated in Fig. 5a and b, respectively, and the extracted kinetic data are presented in Table 5.

4.5. Discussions

Comparing with the three pseudo-components model ($n = 1$), the fit of the DAEM is slightly lower for untreated stump, but somehow higher for torrefied stump. The activation energies extracted from DAEM vary in the range of ±20% comparing with the values generated from the three pseudo-components model ($n = 1$). However, the pre-exponential factors of the DAEM are smaller. The distribution widths (σ) in the DAEM vary in the range of 20–30% of the mean value for hemicellulose, 7–8% for cellulose and 20–40% for lignin. The contribution factors of the biomass components obtained from the evaluation of the models are in good agreement to one another. For example, in the case of the untreated stump, the average mass fractions of hemicellulose, cellulose, lignin obtained from the three-pseudo-component model with $n = 1$ are 33%, 47%, 20%, respectively; and 32%, 49%, 19% from the DAEM.

From the data in Tables 4 and 5, it can be seen that the kinetic parameters for the two first pseudo-components (hemicellulose and cellulose) obtained from the pyrolysis kinetic evaluation at the same heating rate (40 K/min) for the stump torrefied at 200 °C and 250 °C are almost identical compared to that of the untreated stump. However, the contribution factor of hemicellulose reduces with increasing torrefaction temperature. Only the last pseudo-component (lignin) shows a small change for the stump torrefied at 200 °C and a significant change for the sample torrefied at 250 °C. At the torrefaction temperature of 300 °C, the contribution of hemicellulose reduces to zero, whereas the kinetic parameters of cellulose are virtually constant. It can be concluded that increases in the severity level of torrefaction do not affect the kinetics parameters (the activation energy and the pre-exponential) of hemicellulose and cellulose, but reduce the contribution factor of hemicellulose from 32% to 0% and increase the contribution factor of cellulose from 49% to 74%. Lignin is the only

Table 5
Extracted data from the DAEM simulation.

Sample	E_a (kJ/mol)	σ (kJ/mol)	A (s^{-1})	c	Fit (%)
US (10 K/min)	93.79	27.58	8.10E+05	0.35	98.60
	168.44	13.63	2.84E+11	0.51	
	57.55	25.09	1.64E+01	0.13	
US (20 K/min)	104.81	26.39	5.30E+06	0.30	98.77
	176.31	13.65	7.95E+11	0.48	
	48.01	22.40	3.11E+00	0.21	
US (40 K/min)	108.16	25.71	4.77E+06	0.31	99.13
	183.85	13.67	8.16E+11	0.48	
	43.39	21.40	2.74E+00	0.21	
TS 200 °C (40 K/min)	111.19	25.68	8.84E+06	0.30	99.37
	185.79	13.68	1.12E+12	0.54	
	50.70	15.73	8.52E+00	0.16	
TS 250 °C (40 K/min)	125.42	25.25	1.13E+08	0.20	99.05
	190.81	13.97	3.14E+12	0.62	
	64.46	13.22	8.08E+01	0.17	
TS 300 °C (40 K/min)	–	–	–	–	98.75
	221.34	16.10	8.80E+14	0.62	
	60.44	13.26	4.68E+01	0.38	

US: untreated stump, TS: torrefied stump.

component which exhibits changes in its kinetic parameters. However, the trend of the changes is not clear.

It appears that the torrefied stump wood has higher activation energy than the native stump wood. At the heating rate of 40 K/min, the activation energy predicted for the native stump pyrolysis is in the range of 105.2–108.9 kJ/mol, 183.5–183.6 kJ/mol, and 40.3–48.01 kJ/mol for hemicelluloses, celluloses, and lignin, respectively. That for pyrolysis of the stump torrefied at 200 °C is 105.13–111.19 kJ/mol, 183.68–185.79 kJ/mol, and 40.49–50.70 kJ/mol, respectively. For the stump torrefied at the higher temperature, 250 °C, the activation energy for the carbohydrate components is only slightly varied, but that for the lignin component increases quite significantly.

5. Conclusions

Three models were presented and employed for a comparative evaluation of stump biomass pyrolysis kinetics in the kinetic regime. They are the single-reaction model, the three pseudo-components models with first- and n-order, and the DAEM with $n = 1$. It was shown that the single-reaction model was not suitable for simulating stump biomass pyrolysis. The two other models including the three pseudo-components model with $n = 1$ and $n \neq 1$, and the DAEM exhibited very good fits between the simulated and experimental curves. The kinetics data extracted from the simulation using these three models are all in a reasonable range, comparing to the literature [33,35]. In addition, the complexity level in calculation and the simulation time increase following the order from the three pseudo-components model with $n = 1$, three pseudo-components model with $n \neq 1$, and the DAEM. However, the difference in fit quality of the kinetic evaluation is insignificant. Therefore, the three pseudo-components model with $n \neq 1$ is recommended as the most suitable for simulation and prediction of kinetic behaviour of slow pyrolysis for both untreated and torrefied stump, considering that it offers the best fits to the experimental data and that the generated reaction orders are realistic, being slightly higher than unity.

It appears that the torrefied stump has higher activation energy than its native material. The activation energy predicted for the native stump pyrolysis is in the range of 105.2–108.9 kJ/mol, 183.5–183.6 kJ/mol, and 40.3–48.01 kJ/mol for hemicelluloses, celluloses, and lignin, respectively. That for pyrolysis of the stump torrefied at 200 °C is 105.13–111.19 kJ/mol, 183.68–185.79 kJ/mol, and 40.49–50.70 kJ/mol, respectively.

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